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TEMPERATURE DEPENDENCE OF THE HOMOGENEOUS LINEWIDTH OF THE $^5D_0$ - $^7F_0$ TRANSITION OF Eu^{3+} IN AMORPHOUS HOSTS AT HIGH TEMPERATURES

by

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ABSTRACT

The temperature dependence of the homogeneous linewidth of the $^5D_0$ - $^7F_0$ transition of Eu^{3+} in different amorphous solids is determined in the 295 °K to 800 °K temperature range. The nearly quadratic temperature dependence observed is discussed in terms of Raman broadening and mechanisms based on two-level systems known to exist in disordered systems.

INTRODUCTION

Recently there has been much interest in the origin of the optical homogeneous linewidths of rare-earth ion transitions in amorphous materials. Selzer et al.[1] have observed a nearly quadratic temperature dependence of the homogeneous linewidth of the $^5D_0$ - $^7F_0$ transition of Eu^{3+} in a silicate glass from 10 to 100° K. Avouris et al.[2] have reported a similar temperature dependence for the homogeneous linewidth of Eu^{3+} in silicate glass in the 200 -350° K temperature range. Similar results have been obtained for the homogeneous linewidth of Pr^{3+} in BeF_2 and GeO_2 glasses[3] in the 8 - 300° K range. This behavior of the homogeneous linewidth of rare-earth ions in amorphous hosts cannot be accounted for by the usual one or two phonon broadening mechanisms used to account for the linewidth in crystalline hosts. At temperatures $T > 100$ K, the homogeneous linewidth in crystalline hosts show a quadratic temperature dependence[1,3], consistent with a Raman broadening mechanism for $T > 0.3\ T_D$ where T_D is the Debye temperature. At temperatures below 100 K the Raman contribution to the linewidth drops off as T^7. For $T < 100$ K a direct one phonon or Orbach process with a T or exponential dependence on temperature, respectively, dominate[1,3]. The anomalous low temperature behavior in glass hosts is suggestive of an ion-lattice interaction peculiar to amorphous materials.

Lattice models associated with the disorder inherent to amorphous materials, known as two-level systems (TLS), have been used to interpret many of the low temperature properties of glasses[4,5]. Selzer et al.[1] considered the interaction between pairs of these TLS as a broadening mechanism but predicted a linear temperature dependence. Reinecke[6] has

described a line broadening mechanism involving TLS which also predicts a linear temperature dependence. Lyo and Orbach[7] have described a mechanism involving TLS which predicts a T^2 dependence for temperatures below the Debye temperature. At temperatures above the Debye temperature or cutoff in TLS density of states, whichever is lowest, a linear temperature dependence can be expected[7] for the homogeneous linewidth in glasses.

In order to further understand the homogeneous line broadening mechanism in glasses and to test recent theories we have used fluorescence line narrowing techniques[8] to measure the temperature dependence of the homogeneous linewidth of the $^5D_0$ - $^7F_0$ transition of Eu^{3+} in glasses from 295 K to as high as 800 K. Silicate, $Ca(PO_3)_2$, and B_2O_3 glasses with 10, 20, and 30 mole % Na_2O were used. The borate glasses, though similar in composition, are known to undergo significant structural changes[9] with the addition of Na_2O. These structural changes have been shown to affect the spectral properties of Eu^{3+} [10,11]. We have found that the homogeneous linewidth follows a nearly quadratic temperature dependence in all of these glasses in the high temperature range. These results, along with those reported in refs. 1-3, show that a smooth quadratic temperature dependence is effective from 10 - 800° K.

EXPERIMENTAL

Measurements of the homogeneous linewidth were made on five glass samples. Sample compositions were (mole %): 75 SiO_2, 15 Na_2O, 5 ZnO, and 5 BaO for the silicate glass and 100 $Ca(PO_3)_2$ for the calcium metaphosphate glasses with 0.25 and 1 mole % Eu_2O_3 respectively. The borate sample compositions were (mole %): 90 B_2O_3, 10 Na_2O; 80 Na_2O, 20 Na_2O;

and 70 B_2O_3, 30 Na_2O with 0.5 Eu_2O_3 for each of the three samples. Details of the glass preparation are given in ref. 10.

Samples were mounted in an oven for measurements made above room temperature that maintained constant temperature to ± 3° K. An Iron-Constantan thermocouple affixed to the sample was used for temperature measurement. For measurements made below room temperature the samples were held in liquid N_2 vapor warmed by a feedback controlled heating core that stabilized the temperature to better than ± 1° K.

A Quanta-Ray DCR-1 Nd:YAG pumped PDL-1 pulsed dye laser with a spectral width of ~ 0.3 cm^{-1} and a 6 ns pulse width was used as the excitation source. Excitation was made at 5780 Å for all of the samples, corresponding roughly to the maximum of the inhomogeneous profile of the $^5D_0$ - $^7F_0$ transition of Eu^{3+} in these glasses. The emission was dispersed with a 1 M Jarrell-Ash scanning monochromator. Resonant detection required the use of a gated phototube[12] to reject scattered excitation light. Signal averaging was accomplished with gated photon counting with a 3 ms window delayed 50 μsec after the laser pulse. In order to assess the contribution of spectral diffusion or other time dependent effects, the detection gate width was decreased from 3 ms to 50 μsec at various temperatures. No change in the observed lineshape was detected on this time scale.

The observed lineshapes for the silicate glass are shown in Fig. 1 for three different temperatures. At room temperature and below the lineshapes are well fit to a Lorentzian. Well above room temperature deviations from a Lorentzian fit were observed on both wings of the line. On the low energy side, overlap with the $^5D_0$ - $^7F_1$ fluorescence from resonantly pumped $^7F_0$ - $^5D_0$ ions was observed. On the high energy side the intensity falls off more slowly than a Lorentzian. This may be attributed to the $^5D_0$ - $^7F_0$ fluorescence of ions pumped from the thermally

populated $^7F_1$ levels via the $^7F_1$ - $^5D_0$ transition. A discussion of this effect is given in ref. 13.

Deconvolution of the instrumental width from the observed width was done using the table of Hegarty et al.[14] to yield an effective measured width ($\Delta\nu_m$). The homogeneous width ($\Delta\nu_{hom}$) was calculated from the measured width using the approximation[15]

$$\Delta\nu_{hom} = \tfrac{1}{2}\,\Delta\nu_m$$

for $\Delta\nu_m < 2/3\ \Delta\nu_{inh}$, where $\Delta\nu_{inh}$ is the inhomogeneous width of the $^5D_0$ - $^7F_0$ transition which is on the order of 60 - 80 cm^{-1} fwhm for the glasses used in this study. For $\Delta\nu_m > 2/3\ \Delta\nu_{inh}$, the tables of ref. 14 were used.

RESULTS AND DISCUSSION

The results of our measurements of the temperature dependence of the homogeneous linewidth are shown in Fig. 2. The homogeneous linewidth of the $^5D_0$ - $^7F_0$ transition at 5780 Å is found to exhibit a T^α temperature dependence with α equal to 2.3, 1.9, 1.9, 2.2, and 2.2 for the silicate, calcium metaphosphate, and borate glasses with 10, 20, and 30 mole % Na_2O respectively; where each of these exponents is good to $\pm$ 0.3.

The nearly T^2 dependence of the homogeneous linewidth over the measured temperature range is consistent with a two phonon broadening mechanism as has been observed in crystalline hosts[1,3] for $T > 0.3\ T_D$ and conflicts with the high temperature linear dependence predicted by Lyo and Orbach.[7 †] In glass hosts, the smooth continuation of the T^2 dependence of the homogeneous linewidth down to 10 K[1,3], inconsistent with a Raman broadening mechanism based on the Debye model, makes the relative contribution of the Raman mechanism in the high temperature range less clear.

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†These authors arrive at the T^2 dependence by assuming that the density of stat[es] of the TLSs as a function of the zero-point energy difference of the two wells [is] constant on the temperature scale of the experiment. For the temperature range[s] used this doesn't seem reasonable.

Furthermore, the smooth nearly T^2 dependence of the homogeneous linewidth in glasses from 10 K to as high as 800 K, with the same intercept, might suggest that the same mechanism is effective over the entire temperature range.

NMR studies[16,17] of the spin lattice relaxation rate (T_1^{-1}) of ^{11}B and ^{23}Na in sodium borate and silicate glasses over the 1.2 to 300 K temperature range have shown that the ordinary two phonon Raman contribution was negligible over the entire range investigated. Interpretation of these results[16,17] was also made in terms of processes involving TLS. Recent measurements of the homogeneous linewidths of the $^5D_0$ - $^7F_0$ transition of Eu^{3+} in sodium borate glasses at room temperature[10] have shown that the homogeneous linewidth increases linearly with the fraction of tetrahedrally coordinated boron atoms. This work also showed a 3.5 power dependence on the velocity of sound, v_s, for the sodium borate glasses. This is quite different from the v_s^{-10} dependence expected from the ordinary Raman process[18]. The changes in ion-lattice coupling and type of effective TLS[10] with the structural changes associated with the addition of sodium oxide to borate glass may mask the actual velocity of sound dependence. This might suggest that the homogeneous linewidth in glasses is only weakly dependent on the velocity of sound. Pelligrino et al.[19] have observed a $\Delta\nu_{hom} \propto v_s^{-2.6}$ dependence for the homogeneous linewidth of Pr^{3+} in a variety of host glasses at room temperature with deviations observed for borate glasses. These results either indicate that the ordinary Raman broadening mechanism is ineffective in determining optical homogeneous linewidths or else the assumptions implied in deriving the dependence on the speed of sound do not hold for glasses.

At the moment, it is difficult to distinguish between two possibilities: 1) the TLS model[6,7] is operative in the whole range of temperature but that

theoretical high temperature predictions need further examination or else, 2) the Raman process takes over smoothly[†] (from the TLS mechanism) as the temperature increases without obvious breaks in the $\Delta\nu_{hom}$ vs T dependence. It is obvious that more theoretical examination of this problem is needed.

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[†]In the range of $T \leqslant 40$ K, R. P. Stout (Ph.D. Dissertation, Iowa State U. 1981) found that a combination of phonon assisted tunnelling and Raman process fit experimental data in reference 3.

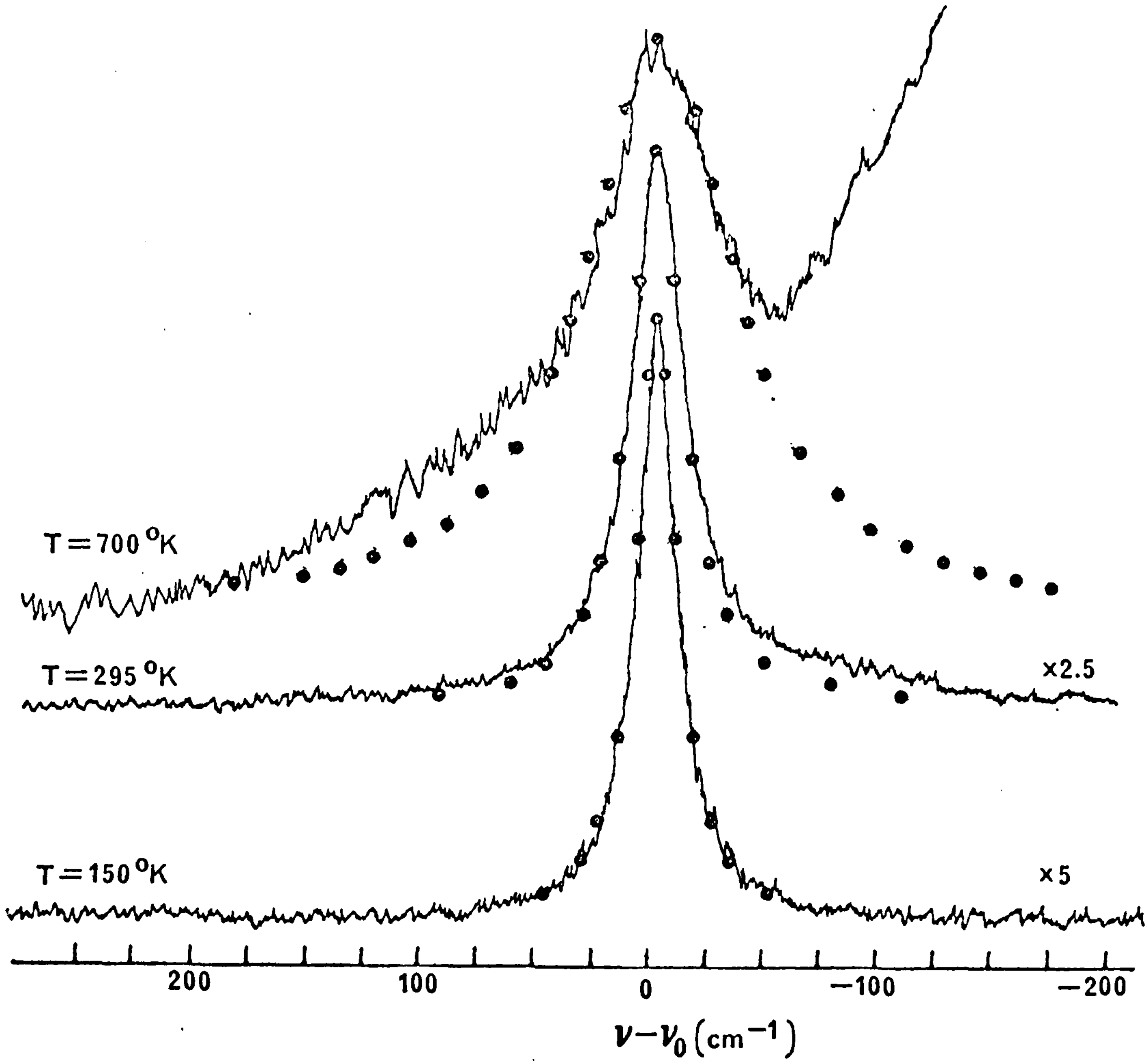
REFERENCES

1. P. M. Selzer, D. L. Huber, D. S. Hamilton, W. M. Yen and M. J. Weber, Phys. Rev. Lett. 36, 813 (1976); P. M. Selzer, D. L. Huber, D. S. Hamilton, W. M. Yen and M. J. Weber, AIP Conference Proceedings No. 31, Structure and Excitation of Amorphous Solids, Williamsburg (1976).
2. P. Avouris, A. Campion and M. A. El-Sayed, J. Chem. Phys. 67, 3397 (1977).
3. J. Hegarty and W. M. Yen, Phys. Rev. Lett. 43, 1126 (1979).
4. P. W. Anderson, B. I. Halperin and C. M. Varma, Phil. Mag. 25, 1 (1972).
5. W. A. Phillips, J. Low Tem. Phys. 7, 351 (1972).
6. T. L. Reinecke, Solid State Commun. 32, 1103 (1979).
7. S. K. Lyo and R. Orbach, Phys. Rev. B 22, 4223 (1980).
8. A. Szabo, Phys. Rev. Lett. 27, 351 (1971).
9. P. J. Bray and T. G. O'Keefe, Phys. Chem. Glasses 4, 37 (1963).
10. J. R. Morgan, E. P. Chock, W. D. Hopewell, M. A. El-Sayed and R. Orbach, J. Phys. Chem. 85, 747 (1981).
11. M. J. Weber, J. Hegarty and D. H. Blackburn, in "Borate Glasses: Structural Properties and Applications," Plenum Press, New York (1978) p. 215.
12. W. Hopewell, thesis, 1980, University of California, Los Angeles.
13. E. Takushi and T. Kushida, J. Lumin. 18/19, 661 (1979).
14. J. Hegarty, R. T. Brondage and W. M. Yen, Appl. Opt. 19, 1889 (1980).
15. T. Kushida and E. Takushi, Phys. Rev. B 12, 824 (1975).
16. J. Szeftel and H. Alloul, Phys. Rev. Lett. 34, 657 (1975).
17. J. Szeftel and H. Alloul, J. Non-Cryst. Solids 29, 253 (1978).
18. B. DiBartolo, Optical Interactions in Solids (John Wiley and Sons, Inc., New York) Ch. 15.
19. J. M. Pelligrino, W. M. Yen and M. J. Weber, J. Appl. Phys. 51, 6332 (1980).

FIGURE CAPTIONS

Fig. 1. The observed (solid lines) and the Lorentzian fit (solid circles) to the homogeneous lineshapes of the $^5D_0$ - $^7F_0$ transition of Eu^{3+} in a silicate glass for resonant emission at 17300 cm^{-1} at different temperatures. No change in the observed lineshape was detected upon decreasing the detection gate width from 3 ms to 50 μs thus ruling out spectral diffusion on this time scale.

Fig. 2. Temperature dependence of the homogeneous linewidth ($\Delta\nu_{hom}$) of the $^5D_0$ - $^7F_0$ emission of Eu^{3+} for several glass host observed with resonant excitation at 17300 cm^{-1}. ○ - silicate; △ - $Ca(PO_3)_2$; □ - 70 mol % B_2O_3, 30 mol % Na_2O; ◇ - 90 mol B_2O_3, 10 mol % Na_2O.


T = 700 °K
T = 295 °K
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×2.5
×5
200
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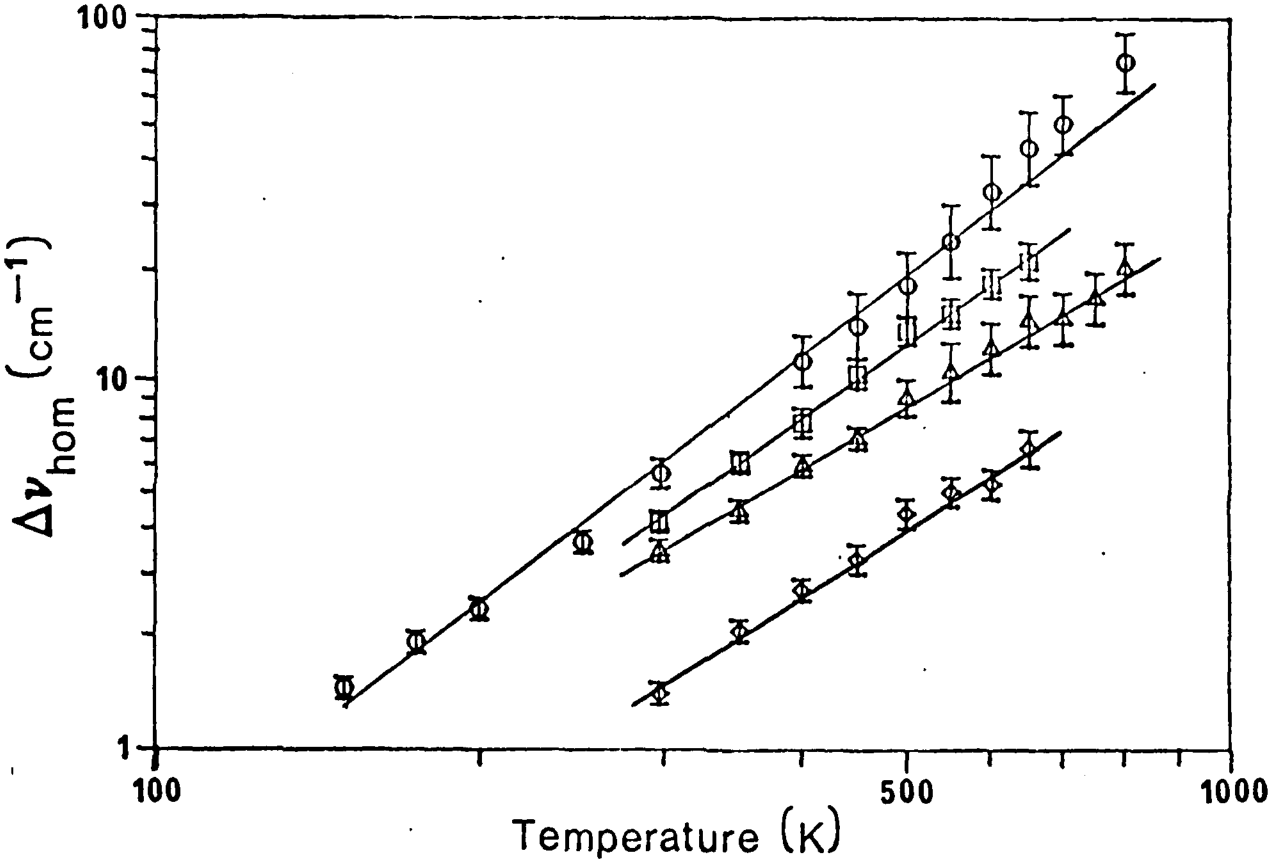

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1
$\Delta\nu_{hom}$ (cm^{-1})
100
500
1000
Temperature (K)

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